THE CHEMISTRY OF SILICA

Solubility, Polymerization, Colloid and Surface Properties, and Biochemistry

RALPH K. ILER

MAR 2 1 2001

faces including surface hydration and reactions, particularly from the standpoint of infrared absorption studies. In 1968, Snyder (10) discussed the structure of the surface of silica with emphasis on the relation to adsorption characteristics and use of porous silicas in chromatography. In 1970, Okkerse (11) in an extended review of the preparation and properties of porous silica described the hydroxylated silica surface and its structure, with the view that at the surface there is probably only one OH per silicon atom, and reviewed data on dehydration. In 1972, Snoeyink and Weber (12) covered the same ground as Boehm, adding newer references. In 1976, Barby (13) contributed a broad survey of "silicas", that is, gels and powders, with a detailed discussion of the nature of the surface silanol groups.

A general survey of the structure and chemistry of oxide surfaces in relation to adsorption was published by Kiselev in 1971 (14). Various aspects of the surface chemistry of silica in contact with water have been surveyed in a general article on the colloid-water interface by Wiese et al. (15).

With these numerous reviews, the question can be logically asked whether still another review here is justified. However, it is evident that most of the emphasis has been on the nature of the hydration of the surface and in no case have the different aspects of the surface chemistry, including behavior in contact with water and organic compounds, been made available in one convenient place.

NATURE OF THE SILICA SURFACE

Many diverse chemical and physical methods for examining the composition and structure of the surfaces of solids are now available. These have been described in some detail by Kane and Larrabee (16). Many of these are more suitably applied to macroscopic surfaces than to powders and colloids, but among them are some that have not yet been used in studying silica. In this chapter, emphasis is placed on what has been learned about the surface chemistry rather than on the methods used, since these are available in cited references.

A very effective summary of the nature of the silica surface as known in 1965 was presented by Hockey (17). A more recent survey is that of Boksanyi, Liardon, and Kovats (18) with regard to attaching organosilyl groups to the surface.

Structure of the Underlying Silica

Though it has been found that different forms of silica appear to act alike in regard to the adsorption of water (6), it would certainly be surprising if the SiOH groups on clean surfaces of all the different crystalline and amorphous forms would behave exactly the same. Indeed Stöber (19) has shown that the SiOH groups on the rare, extremely dense form of silica, stishovite, in which each silicon is coordinated with six oxygen atoms, act as those on alumina do as far as hydrogen bonding is concerned. Stishovite adsorbed polyvinylpyridine$N$-oxide only very weakly whereas the other forms of silica surfaces adsorbed it strongly. Since there are some density

differences, for example, between quartz and amorphous silicas, we would expect some small differences to exist. However, work by Meyer and Hackerman (20) seems to show that particles size or radius of curvature of the surface may be a more important variable than differences between the amorphous and ordinary crystalline states of silica.

Definition of Surface

The term surface will be understood to mean the boundary of the nonporous solid phase. By custom, the "surface" usually means the boundary that is impervious to nitrogen, the adsorbate most commonly used to measure the surface area. However, there are micropores into which water but not nitrogen can penetrate. Since the area in micropores is difficult to define, the "surface" will generally be understood to mean that which is measured by the usual BET method of nitrogen adsorption.

Even a small amount of impurity, if located on the surface, can greatly modify surface properties. For example, if 100 ppm of sodium impurity in a silica gel having a specific surface area of 200 $m^3 g^{-1}$ were all located on the surface, there would be one sodium atom per 100 nm^2. The atoms would be only 10 Å apart if evenly distributed. Fowkes and Burgess (21) showed that the surface of silica traps sodium atoms. Even the purest quartz collects 10^{15} cm^{-2} atoms within 100 Å of the surface. This creates a negative oxide ion charge at the surface. If the surface layer is etched off with HF it becomes uncharged, but after some weeks at room temperature more sodium comes from the interior. A bulk concentration of 2 ppm Na can result in 2% sodium on the surface after annealing at 1000°C. Since silica containing 2 ppm is considered extremely pure, it can be seen that in most gels and precipitates, sodium may play an unrecognized role.

The Hydroxylated Surface

Since the silicon atoms on the surface of amorphous silica are, by definition, not in an exactly regular geometrical arrangement, it is obvious that the hydroxyl groups attached to these silicon atoms will not be exactly equidistant from each other (Figure 6.1). They are therefore not all equivalent either in their behavior in adsorption or in chemical reactions.

Also, in aqueous solution it can be imagined that extra monosilicic acid molecules might condense with the surface to give attached silicon atoms with two or even three attached hydroxyl groups, as shown in Figure 6.1 at F and G. Although these groups have been postulated to explain certain data, it is probable that they condense further leaving only SiOH groups on the dried surface.

On silica dried from water, the hydrogen-bonded water molecules as in Figure 6.1 come off in vacuum at ordinary temperature or at 150°C in the atmosphere.

The silanol number, that is, the number of hydroxyl groups per unit surface area, has been a matter of much research and discussion. It was observed by Belyakova
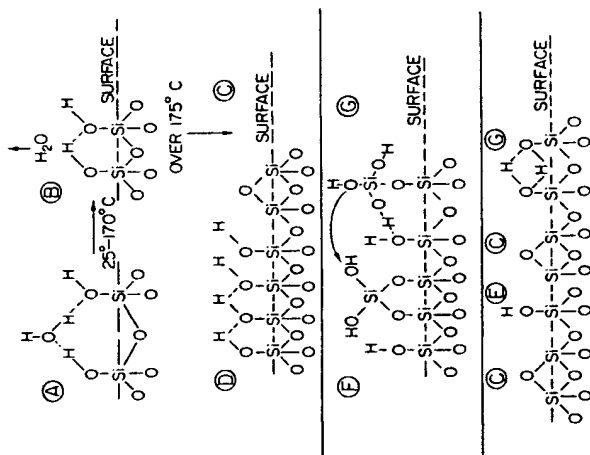
Figure 6.1. Postulated types of hydroxyl groups on the surface of amorphous silica. *A*, vicinal hydrated; *B*, vicinal anhydrous; *C*, siloxane—dehydrated; *D*, hydroxylated surface; *E*, isolated; *F*, geminal; *G*, vicinal, hydrogen bonded. *Note: F* and *G* probably do not actually exist on a dried surface.

al. (6) that the silanol number was about the same on different types of silica. On the other hand, quite diverse results were reported by other workers. As pointed out by Dubinin, Bering, and Serpinskii (22) in 1964, in the surface of different samples of amorphous silica made in different ways, the packing of the tetrahedra of oxygen atoms, each containing a silicon atom, is not regular and can vary. When silica particles are formed in water the number of OH groups can be affected in several ways as shown in Figure 6.2:

1. "Buried" uncondensed SiOH groups below the surface of the siloxane network give rise to distortions at the surface and when deeper can be removed only at high temperature.

2. Some SiOH groups can be located just within the surface and increase the average packing density of OH groups per unit surface area as at *B*.

3. On particles with small radii, the curved surface with a positive radius of character tends to hold SiOH groups farther apart so they can form fewer hydrogen bonds between them, making them more readily removable at higher temperature, as at *C*, as compared with *D*.
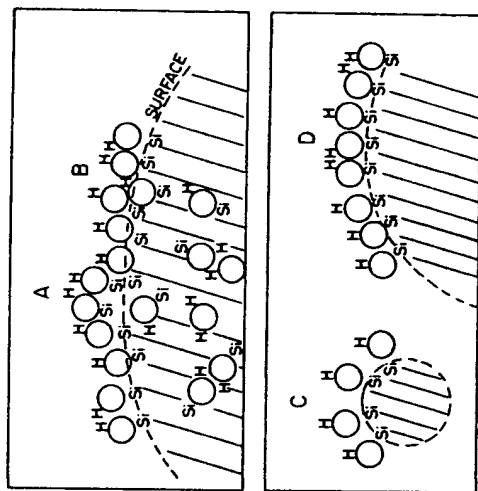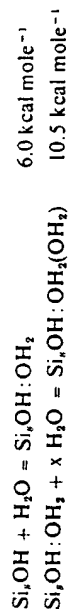
Figure 6.2. Factors affecting the number of hydroxyl (silanol) groups in and on a sil... particle formed in water. *A*, buried hydroxyl distorts the surface, facilitating presence geminal silanol groups; *B*, hydroxyl group just below surface is more stable and increa... number per unit area; *C*, hydroxyl groups on very small (under 100 nm) particles are l... crowded per unit area; *D*, hydroxyl groups on a larger particle are closer together and can fo... more stable hydrogen-bonded pairs.

4. Conversely, in crevices at points of contact between particles where there i... negative radius of curvature, for example, in micropores, the surface OH gro... are brought closer together by the curvature and dehydration is more difficult.

5. In particles formed at low temperature and low pH by aggregation of still smal... particles there are micropores or submicropores as described in Chapter 4, w... hydroxylated surfaces in which water is strongly retained. Such surfaces are r... measured by the BET method because nitrogen cannot penetrate so that t... concentration of OH per square nanometer appears abnormally high.

State of Water at the Hydroxylated Surface

In a detailed study of the behavior of water at the silica surface, dehydrated 700°C, Klier and Zettlemoyer (23) have shown that water sits "oxygen down" the SiOH groups, at least at the beginning stages of adsorption. Then hydroge... bonded clusters of H_2O molecules may be formed even before all the SiOH grou... have adsorbed H_2O molecules to form $Si_sOH:OH_2$ groups. This means that... isolated SiOH groups water is less strongly absorbed than on top of other wat... molecules already adsorbed.

$$Si_sOH + H_2O = Si_sOH:OH_2 \qquad 6.0 \text{ kcal mole}^{-1}$$
$$Si_sOH:OH_2 + x\, H_2O = Si_sOH:OH_2(OH_2) \qquad 10.5 \text{ kcal mole}^{-1}$$

It is probable that the hydrogen-bonded water represents the adsorption of water only on those silanol groups that are not strongly hydrogen bonded to adjacent groups.

Nmr has been used by Mank, Baran, and Yankovskaya to distinguish labile protons and OH groups on the silica surface and OH groups within the particles (53a). The spacing of SiOH groups was estimated to be 5.0–5.4 Å, which would correspond to about 3.9 OH nm^{-2} if distributed on a hexagonal grid, or 3.7 OH nm^{-2} if on a square grid. Kvlividze (53b) in 1964 listed prior references and published nmr studies on wide-pored gel dehydrated in vacuum at 200°C. The adsorption of water was followed and measurements made at low temperature from 83 to 273°K.

Internal Hydroxyl Groups and Trapped Water

As investigations continued it became clear that in almost all kinds of amorphous silicas there are silanol groups not only on the surface but throughout the particle structure. These trapped silanol groups arise in different ways depending on the process by which the particles were formed.

In pyrogenic silicas, as discussed in Chapter 5, the spherical particles of the order of 10–20 nm in diameter were formed by aggregation of elementary particles only 1–2 nm in size condensed from the flame. These contain some surface SiOH groups which become locked within the final particle which sinters nearly to theoretical density before it cools.

In silica gel made from sodium silicate the primary polysilicic acid particles are usually 2–3 nm in size when they aggregate and in the course of "aging" the gel some SiOH groups become trapped as particles coalesce. Cornier, Baverez, and Bastick (54) showed that surface groups can indeed be trapped when silica gel is highly compressed.

In the case of particles grown by autoclaving in water at high temperature it might be thought that the silica network structure would densify and rid itself of internal SiOH groups. However, Davydov and Kiselev (55) showed that, in fact, water remains within the structure. When driven out it may leave micropores as discussed in detail by Kiselev (14).

When colloidal particles are formed in solution by the "buildup" process as described in Chapter 5, the pH is about 9 and a certain small number of sodium ions are adsorbed at the same time that silica is deposited on the growing particles. These are associated with water and even after they are removed by prolonged acid treatment and ion exchange, a few strongly held water molecules or silanol groups remain deep in the structure.

Still another source of internal SiOH groups is diffusion of H_2O into the solid SiO_2 structure. Doremus (56) states that just as H_2O diffuses into vitreous silica at high temperature, it can penetrate amorphous SiO_2 to a distance of 150 Å where a small amount can exist as SiOH pairs.

It was rather unexpected to find that pyrogenic silicas which had condensed from a flame still contained micropores. Thompson (57) showed by infrared studies that there is a small but significant volume of micropores ranging up to 0.01 cm³ g^{-1}

which hold water very strongly. Water was removed from the outer surface of silica particles by pumping under high vacuum at 26°C, but not from capillaries where water is probably strongly hydrogen bonded to opposite sides of capillary walls. This water continues to come off up to 400°C but above this temperature the capillaries become closed by formation of Si-O-Si bonds and are not subsequently opened up by rehydration.

Some data by Uytterhoeven, Hellinckx, and Fripiat (58) revealed that on pyrogenic Aerosil at 100°C, only 35% of the SiOH groups were on the surface, and on a xerogel only 61%. On the other hand, when silica particles are grown gradually by the deposition of soluble silica in hot alkaline solution it would be expected that fewer hydroxyl groups would be trapped in the structure. However, no real evidence has been advanced to show that this is so. It could possibly be shown by comparing total hydroxyl groups versus surface area for particles of different sizes, all made in the same way. The OH content should extrapolate to the value for the internal concentration with very large particles where the surface becomes negligible.

When silica is autoclaved in water at high temperature water diffuses into the solid phase to reach an equilibrium concentration. According to Chertov et al. (59), after being autoclaved silicas with surface areas of 21–600 m² g^{-1} contain 1 meq of internal water per gram of SiO_2, which would be about 0.9%. During autoclaving the surface area was reduced but the surface hydroxyl concentration remained at 5.6 OH nm^{-2}. However, the bulk water content of 0.9% was constant (60).

From this it is obvious that in calculating the number and behavior of silanol groups on the surface, the internal groups must not be included. Unfortunately this has not been done in many investigations. It was only after it was realized that the internal bound water could be driven out at high temperature and the resulting micropores closed that silica samples were obtained on which dehydration and rehydration studies could be carried out reproducibly. Even then for unequivocal results it is necessary to measure the surface hydroxyl groups by a method that responds only to the SiOH groups on the surface.

The presence of internal H_2O (or SiOH groups which probably occur in pairs as H_2O hydrolyzes internal Si-O-Si linkages) also has confused the infrared studies. Both internal and external SiOH groups give absorption bands. In particular, the assumption of geminal hydroxyl groups [=Si(OH)$_2$] on the surface to explain the high liquid water content of previously unheated silica is now debatable. Internal uncondensed silanol groups appears to be a more likely explanation.

Hydroxyl Groups per Square Nanometer

It now seems generally agreed that on the smooth, nonporous heat-stabilized amorphous silica surface that is fully hydroxylated there are 4–5 SiOH groups nm^{-2} (100 Å²) which remain when the sample is dried at 120–150°C.

This value is cited in most of the summary papers (4–13). Such a surface is obtained after heating the powder or gel to elevated temperature to drive of internally held water and OH groups and close the pores, then rehydrating in water.

On rehydrated pyrogenic silica Armistead et al. (61) showed that out of 4.6 OH

nm^{-2} on the surface, 1.4 ± 0.1 were free hydroxyl groups not hydrogen bonded to neighbors, and 3.2 ± 0.1 were mutually hydrogen-bonded pairs. In addition, there were 1.6 OH nm^{-2} internal SiOH groups which were irreversibly removed upon annealing.

Type of Group	Identifying Absorption Band (cm⁻¹)
Single OH on surface	3750
Paired OH's on surface	3540
Internal OH's, hydrogen-bonded	3650
Molecular H₂O	3400, 1627

Deuterium of heavy water exchanges only with the hydrogen atoms of hydroxyl groups on the surface but not with those in the interior of silica. Zhuravlev et al. (62) compared the weight loss on ignition with SiOH groups on the surface as revealed by deuterium exchange on silica with area of 340 m^2 g^{-1} and 110 Å pore diameter. They found more total water than was bound as surface hydroxyl groups, which amounted to 5.2 OH nm^{-2}.

Results by deuterium exchange as well as those by chemical methods using LiCH₃ or MgCH₃I have been summarized by Davydov, Kiselev, and Zhuravlev (43) and are included in Figure 6.3 and Table 6.1. Later Agzamkhodzhaev et al. (63) used this method on a series of hydroxylated gels, aerogels, and other silicas of different pore sizes and found the surface concentration ranged from 4.2 to 5.7 OH nm^{-2}. Using a similar method Madeley and Richmond (64) found that on four silicas with surface areas of 374–701 m^2 g^{-1} the range of OH nm^{-2} was only 4.27–4.63, with no trend noted. This appears to be the method of choice since exchange is apparently limited to the surface. The surface area is best determined by krypton adsorption using the BET method since results are less affected by the nature of the surface than when nitrogen is used. The exchanged H₂O–D₂O mixture is analyzed by mass spectrometry.

Wirzing (50, 65) showed that the number of OH groups can also be determined by adsorbing water on the OH groups and measuring the resulting unique infrared absorption band at 5265 cm^{-1}. A well-sintered sample of silica powder (Mallinckrodt) that had been repeatedly heated to 800°C, cooled, and rehydrated eight times, with an area of 166 m^2 g^{-1} and obviously free from micropores, was examined. After drying at 120°C it had 5.2 OH nm^{-2} by ignition and 4.0 by this infrared method. On an aerogel the value was 4.4.

On silica that has *not* been heat treated, according to De Boer and Vleeskens (66), there were 6.2 OH nm^{-2} but after repeated wetting, heating, and drying, the surface became smoother on an atomic scale so that the value 4.6 ± 0.2 OH nm^{-2} was reached. On the dry, fully hydroxylated surface about half of the silanol groups are present as hydrogen-bonded pairs. In such a random distribution of surface groups it is evident that many SiOH groups will remain single and unpaired (67).

The hydroxylated surface, with adsorbed water, has two types of H₂O and two of SiOH, according to Anderson and Wickersham (68). A monomeric H₂O molecule
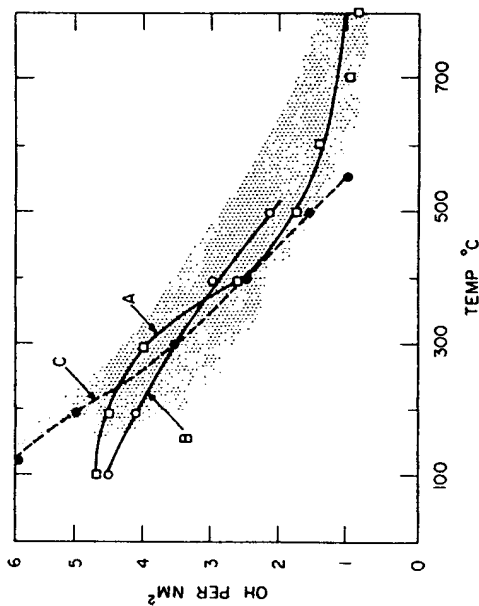
Figure 6.3. Dehydroxylation of the silica surface versus temperature: Shaded area: range of data on a variety of types of silica by Davydov, Kiselev, and Zhuravlev (43). Dehydration of annealed (700°C) and rehydrated silica. *A*, in air; *B*, in vacuum. [Based on Taylor, Hockey, and Pethica (84).] Broken line *C*, data on silica, not annealed. [From Uytterhoeven et al. (83). Fripiat et al. (47), Zhuravlev and Kiselev (85), and Taylor, Hockey, and Pethica (84,86).]

may be bonded to a single SiOH. A cluster of H₂O molecules may form a hydrogen-bonded network. There can be nonbonded SiOH groups and SiOH groups bonded to H₂O molecules.

Proton nuclear magnetic resonance (pmr) was used by Bermudez (69) to determine the number of surface silanol groups even when the surface was covered with up to three monolayers of adsorbed water. The gel had a surface area of 800 m^2 g^{-1} and the silanol concentration was found to be 7×10^{-6} mole m^{-2} or 4.2 OH nm^{-2}.

As will be discussed in connection with dehydration and rehydration of the silica surface, much of the past data showing more than 4.6 OH nm^{-2} is probably due to the presence of internal SiOH groups which were assumed to be on the surface.

Determining the number of OH groups on the surface by chemical methods has given inconsistent results, according to Boehm (8). He points out that by most chemical reactions, for example, esterification or chlorination, only about half of the number of OH groups appear to react, out of the 5 OH nm^{-2} known to be present by determination of active hydrogen or water loss.

It may be that these substituent groups are too large to be accommodated at every former SiOH site. When the substituent group such as ethoxy or chlorine is slightly larger than OH, only about every other OH group can be substituted since the positions of the underlying silicon atoms are fixed. However, the methyl group is small enough to fit in. As reported elsewhere, between four and five methoxy groups per

square nanometer *can* be attached to the surface. This is also why the use of CH₃Li and CH₃MgI by Fripiat et al. (47) has been successful. Another methylating agent is the dimethylzinc complex with tetrahydrofuran (ZnMe₂ · 2THF) used by Hanke (70), who measured the OH concentration on the surface of an aerosil by measuring the volume of CH₄ evolved.

The only other negative substituent small enough to replace all the OH groups is the fluorine atom, but the SiF surface is not easy to develop without attacking the SiO₂ structure.

Triisobutylaluminum in heptane was used by Liefländer and Stöber (71) to react with the surface SiOH. After thorough washing with heptane to remove excess reagent, the surface retained 5.7 micromoles Al on the surface after hydrolysis:

$$Si_sOH + AlR_3 \xrightarrow{-RH} Si_sOAlR_2 \xrightarrow{+H_2O} Si_sOAl(OH)_2 + 2\ RH$$
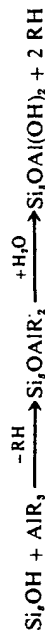
Theoretical Concentration of Surface Hydroxyl Groups

Calculation of the silanol number of the silica surface can be approached in several ways. The simplest is that proposed by Iler (3) based purely on geometric considerations and the density of amorphous SiO₂. This has been described in Chapter 1 and leads to the conclusion that there should be 7.8 silicon atoms nm⁻² at or very near the surface. He assumed originally that there should thus be 7.8 SiOH groups nm⁻² of surface. However, Boehm (8) pointed out that since all the silicon atoms cannot be exactly at the boundary, some must be above and some below, and hence only half of the silicon atoms would bear OH groups so that there would be only 3.9 OH nm⁻².

Iler also suggested that since the density and refractive index of amorphous silica is close to that of cristobalite and tridymite the concentration of surface hydroxyls might be estimated from the crystal structures. The 1.0.0 crystal plane of beta cristobalite that was selected led to the conclusion that on each 50.2 Å² of surface there were two lower level silicon atoms bearing no hydroxyls and two upper levels each bearing two hydroxyl groups, giving 8 OH nm⁻². A similar calculation for the tridymite surface gave 4.6 OH nm⁻². This has been further considered by Peri and Hensley (67), who pointed out that if the 1.0.0 of cristobalite is considered each silicon atom would hold two hydroxyls, making about 8 OH nm⁻², but if these were removed in pairs randomly by a Monte Carlo method there would remain 4.56 OH nm⁻² as either geminal or vicinal pairs.

Since the early experimental data then available (Table 6.1) indicated a value of about 8 OH nm⁻², it was assumed that the higher figure was more probable. This was given some support by Belyakova, Dzhigit, and Kiselev (72) and Zhdanov and Kiselev (73), who found as much as 12 micromoles OH nm⁻² or 7.2 OH nm⁻². However, De Boer and Vleeskens (74, 75) then pointed out that since beta cristobalite crystallizes in octahedra, the hydroxyl concentration should be calculated from the 1.1.1 plane of the octahedral face. This surface is represented in Figure 6.4. The calculated hydroxyl group concentration is 4.55 OH nm⁻². Experimental data confirmed this result.
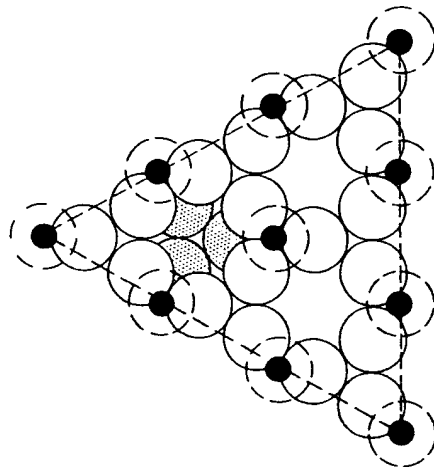
Figure 6.4. Atomic arrangement of the (1.1.1) octahedral face of cristobalite: 4.55 SiOH nm⁻². Large circles, oxygen atoms; small circles, silicon atoms at surface; dashed circles, position of hydroxyl groups on the surface, attached to the underlying silicon atoms. The atomic sizes are not to scale.

From subsequent data it now appears that the heat-stabilized surface of amorphous silica does closely resemble the octahedral face and 4.6 OH nm⁻² is a commonly observed value for rehydrated silicas that have been "smoothed" or annealed at high temperature, then fully rehydrated and dried.

Dehydration and Rehydration

As the temperature is raised, hydroxyl groups condense to form siloxane bonds and water is evolved. The reduction in hydroxyl groups on the surface with increasing temperature has been widely studied and the results have been summarized by Barby (13), Okkerse (11), and Strelko (76), who furnished 168 references.

The phenomenon can be studied by starting with a thermally stable, fully hydroxylated surface and following the removal of hydroxyl groups as water is evolved in a stream of air or nitrogen or a vacuum. Since water vapor strongly catalyzes rearrangement of siloxane bonds, it is not surprising that dehydration data are difficult to reproduce unless the water vapor is removed by vacuum or unless the sample is small and spread in a thin film to permit rapid escape of vapor.

An opposite approach would be to start with a pristine silica surface created in an inert gas or vacuum. Fused quartz has been pulverized in a vacuum by Antonini and Hochstrasser (77), who used electron spin resonance (esr) to study the broken bonds. Si⁺ sites were created and they reacted with CO₂ to give a Si⁺CO₂⁻ complex. The surface loses its activity as it picks up water or other impurities from within the

sample. Zhdanov (78) reported that hydration of the surface was much faster than in the case of surface dehydrated at high temperature.

Kautsky and Michel (79) apparently prepared a form of silica, the surface of which is free from silanol groups, by the oxidation of siloxane, $Si_6O_3H_6$. Unlike ordinary hydrated silicas, this form of SiO_2 did not absorb rhodamine dye to give a fluorescent product.

Probably because of the difficulty of obtaining completely hydrogen-free, finely divided silica of sufficient uniform and high specific surface area, few hydration studies appear to have been made. Such silica might be obtained by vaporizing and condensing SiO_2 in a dry oxygen atmosphere.

Pristine fibers of fused quartz containing 3% B_2O_3 were used by Dietz and Turner (80) for such studies, although the presence of boron in the surface may confuse the picture. The most significant observation was that rehydroxylation of the anhydrous surface is followed rapidly by adsorption of water molecules on the newly formed silanol surface. Also, when the surface is dehydroxylated at 800°C, rehydration is much slower than when dehydroxylated at a lower temperature, but can still proceed. "Nucleation sites" for rehydration are postulated and these become fewer at higher temperature.

Dehydration

Probably hundreds of studies of dehydration of silica have been made but few permit accurate assessment of the degree of dehydroxylation of the silica surface as the temperature is increased. Data are not especially consistent but that should not be surprising since silicas vary so enormously in structure, and also in trace impurities. For example, the presence of some K^+ ions on the silica surface can lower the dehydroxylation temperature by 100–200°C (81).

Since the dehydration is a nonequilibrium process, the *rate* at which water is lost at any stage is a function of temperature and the concentration of remaining silanol groups. Thus to obtain a significant value for OH nm^{-2} at a given temperature, the time of heating or final minimum rate of water loss should be defined. However, there is a relatively rapid loss of water for the first 6–10 hr after the temperature is raised to a new level and then a much slower loss that can go on for days. Usually dehydration is carried on for a fixed time after which, experience has shown, only a "slight" further change occurs.

Different types of silica may have different packing densities of the SiOH groups on the surface and different thermal stabilities of these groups, as pointed out by Imelik and co-workers (82). However, the number of silanol groups per square nanometer on a wide variety of silicas, measured so as to include only those groups on the surface and not in the interior, after being heated to a given elevated temperature, is shown in Figure 6.3.

In the higher temperature range the concentration of residual SiOH groups was measured by Curthoys et al. (87) as follows:

Temperature (°C)	OH nm^{-2}
700	1.2
800	0.9
900	0.65
1000	0.4

As a general rule, starting with a fully hydroxylated surface, there are about 5 OH nm^{-2} at 150°C, and at 800°C only about 1 OH nm^{-2}. Silanol groups start to condense and evolve water extensively above about 170°C. At 400°C somewhat less than half of the hydroxyl groups have been removed so that most of the hydroxyl groups are still adjacent to at least one other. These can adsorb water and thus the surface is readily rehydrated. Above 400–450°C, more hydroxyl groups are removed, leaving larger siloxane areas that are less readily rehydrated (88). At about 750°C only free, unpaired SiOH groups are present at a concentration of 1.3 OH nm^{-2} as shown by Thorp (89) by dielectric isotherms and other methods.

The possibility of thermally dehydrating the silica surface without loss of area was shown by Dzisko, Vishnevskaya, and Cheslova (90). They were probably the first to correctly conclude that physically adsorbed water was removed at 115°C and that most of the remaining "bound" water was present as a layer of hydroxyl groups on the surface because the percent of "bound" water was proportional to the specific surface area. They also concluded that between 115 and 600°C an increasing number of hydroxyl groups condensed with liberation of water and minimum loss of surface area. They estimated that each OH group occupied 15 Å, so that there should be 6.7 OH nm^{-2}.

According to Boehm (8), since distances between OH groups differ on the hydroxylated surface, some OH groups are closer together and stronger hydrogen bonds are formed between them. These show infrared absorption at 3520 cm^{-1}. Others are further apart and are more weakly hydrogen bonded, and show absorption at 3660 cm^{-1}. When heated, the OH groups that are *not* so strongly hydrogen bonded to each other come off first; that is, the 3660 peak recedes first (91–94).

The absorption peaks have been identified as follows:

Type of OH Group	Peak (cm^{-1})
Isolated, single SiOH or "free" hydroxyl groups	3745–3750
Isolated pairs of adjacent SiOH groups (vicinal) mutual hydrogen bonded	3650–3660
Adjacent pairs of SiOH groups with hydrogens bonded to each other	3540–3550
Water molecule adsorbed on the above	3400–3500

Hair (9) summarized the investigations of the silica surface by infrared absorption techniques and described how the various bonds came to be identified.

Kondo and Muroya (95) have observed individual stages in the dehydration process using differential thermal analysis combined with thermogravimetric analysis and infrared absorption measurements. These steps are accompanied by disappearance of an infrared absorption band:

Temperature (°C)	Disappearing Band (cm^{-1})
300	3230
400	3460
500	3620

The band for isolated SiOH groups at 3750 cm^{-1} remains up to higher temperature.

In view of the undoubted presence of internal hydroxyl groups it is not possible to determine what changes these steps represent. It would be very interesting to repeat the study with a sodium-free aerogel which has been heat stabilized at 1000°C and rehydrated by boiling in water for a day or so. Such a silica with much less internal hydration should have a surface area of 100–200 m^2 g^{-1} which might still be sufficient for the above types of measurements.

Kunawicz, Jones, and Hockey (96) and Bermudez (49, 69) indentified the different types of silanol groups by their reactions with BCl$_3$. Other reactions by which silanol groups have been studied are summarized in a later section.

De Boer and Vleeskens (37) found that when the silica is heated to 650°C and cooled and rehydrated in liquid water at 90°C and again dried at 120°C, the OH nm^{-2} value is somewhat lower. If the process is repeated, it reaches 4.6 OH nm^{-2}. If the original SiO$_2$ is heated only once to 890°C and rehydrated and dried the value is 4.6 OH nm^{-2}.

In this way it was demonstrated that a smooth annealed silica surface, when fully hydrated, had one OH per surface Si atom and a concentration of 4.6 OH nm^{-2}. It also showed that while the surface was being annealed, the internal water and/or OH groups were being removed and the structure densified so that less water reentered during the rehydration of the surface.

It was concluded by Okkerse (11) after reviewing the available information that *there is no real evidence for the existence of the postulated geminal* $\equiv$Si(OH)$_2$ *groups, and certainly not for* –Si(OH)$_3$ *on any dried silica surface. If a silica has an apparent hydroxyl content of more than 4.6 OH nm^{-2}, the excess water must be present as internally trapped water of SiOH groups.*

The internal water and hydroxyl groups has been shown by Chertov et al. (60) to be removed starting at 200°C; the maximum rate per degree temperature rise is at about 500°C for all silicas. However, for more nearly complete removal, the temperature must be around 1000°C. At this temperature, the surface also is largely dehydrated to the siloxane condition.

The mechanism of dehydroxylation has been considered by Hockey and Pethica (97). They point out that it is most likely that there is a migration of protons rather than hydroxyl groups. They propose that protons migrate via strained oxygen

bridges. It would be interesting to determine whether dehydration will proceed more rapidly in the presence of a *low* concentration of water vapor than in a vacuum.

There is some evidence by Kondo, Fujiwara, and Muroya (98) that when the sodium ion content of a gel is increased from 5 to 60 ppm, dehydration is somewhat facilitated. The most obvious effect is lowering the sintering temperature at which rapid loss of surface aea occurs, but in all cases, there is little sintering below 700°C. In the case of the lowest sodium content the concentration of hydroxyl groups as OH nm^{-2} followed the upper limit of the shaded area of Figure 6.3.

For absolute dehydration of porous silica, heating in dry chlorine at 600–1000°C is very effective. This appears to be necessary to obtain glass completely free of silanol groups for optical purposes (99). Another approach is to react the silica such as Aerosil with SiCl$_4$ at 400°C and then heat to 700°C. The resulting surface is essentially free of OH groups (100).

Dehydration of the surface of *crystalline quartz* might be expected to be more uniform since all points on the surface should be chemically alike (except for edges). Stöber (101) studied this phenomenon using quartz particles of different sizes and concluded that at least on the surface of quartz, dehydration occurs in the stages shown in Figure 6.5. Stöber found that even after thorough outgassing at 100°C, one molecule of extremely tightly adsorbed water is retained for each two silanol groups on the quartz surface. This appears to be quite different from the behavior on amorphous silica. It suggests a powerful hydrogen-bonding capacity of the SiOH groups on the surface and is possibly related to the peculiar power of this crystal surface to adsorb multilayers of monosilicic acid from solution as shown by Baumann and described in Chapter 1, Ref. 151.

Another indication of a major difference between the surface of amorphous silica and quartz is furnished by Young and Bursh (102a), who found that the heat of
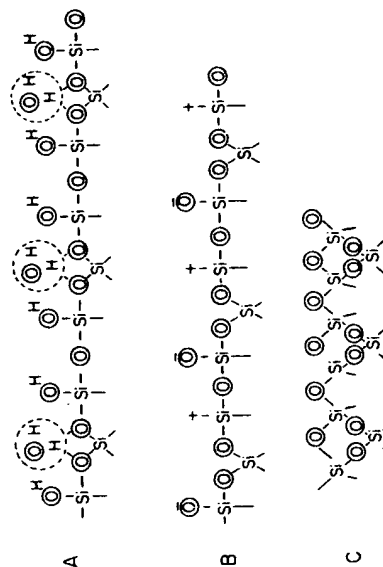

Figure 6.5. Stages in the dehydration of the surface of crystalline quartz. *A*, water irreversibly adsorbed on the quartz surface; *B*, quartz surface immediately after thermal dehydration; *C*, anhydrous siloxane surface after thermal dehydration. [After Stöber (101).]

The Surface Chemistry of Silica

adsorption of water on anhydrous quartz surface is about twice that on amorphous silica, that is, 285 versus 120–190 ergs cm⁻².

Egorov and associates (102b) presented an interesting outline of the nature of the hydration and dehydration of the surface, and observations relating these processes and the specific surface area of silica and also its absorptive properties.

EFFECT OF PARTICLE SIZE AND PORE DIAMETER. According to Brunauer, Kantro, and Weise (103) and confirmed by Whalen (104), small particles such as a particle diameter of 3.7 nm are surface dehydrated at lower temperature than larger ones such as 6.4 nm. Whalen found that silica with an area of 330 m² g⁻¹ held 7 OH nm⁻² at 110°C, and one with 650 m² g⁻¹ held 5.5 OH nm⁻².

Gels with pore diameters of 10, 20, and 27 Å were dehydrated at a series of temperatures by Dzis'ko, Vishnevskaya, and Chesalova (105) and the remaining water contents measured. The ones with smaller pores retained the most water as shown in Table 6.2. These results are explainable on the basis that when the surface hydroxyls are hydrogen-bonded to each other, they are less readily removed at high temperature. It is probable that the dehydration mechanism involves thermal dissociation of a proton which migrates and combines with a hydroxyl group forming water. Such dissociation would require more energy if the proton, that is, hydrogen, was shared between adjacent oxygen atoms.

The effects of particle size where the radius of curvature is positive and of pore diameter where it is negative are shown in Figure 6.6. It seems logical that on the inside of a small pore, the OH groups should be closer together and thus stabilized by hydrogen bonding; other forces can probably also be invoked.

As silica gel is dehydrated, the relative ratio of single (free) hydroxyl groups to adjacent hydrogen-bonded (reactive) hydroxyls is closely related to pore diameter, as recognized by Snyder (10). He stated that the surface of a wide pore is more like that of "crystalline" silica and thus will contain more free hydroxyls. It is not a matter of crystallinity but of geometry. Crystal faces are flat and in this regard are similar to the surface in a large pore which approaches the "flat" condition when viewed on an atomic scale. In small pores with diameter less than 100 Å the negative

Nature of the Silica Surface
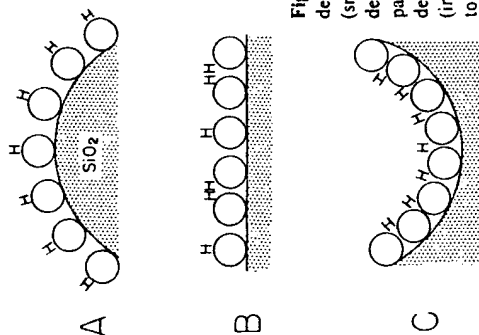
Figure 6.6. Effect of curvature of the silica surface on dehydroxylation. A, small positive radius of curvature (small particles) fewer hydrogen bonds, most easily dehydroxylated; B, large radius of curvature (large particles, flat surface) more hydrogen bonds, less readily dehydroxylated; C, small negative radius of curvature (in small pores), most hydrogen bonding, most difficult to dehydroxylate.

curvature brings the silanol groups closer together so there can be more mutual hydrogen bonding and greater stability toward removal at high temperature.

Snyder and Ward (106) presented data relating S_r/S_1, the fraction of total hydroxyl groups that are highly reactive, to pore diameter. The pore diameter has little effect until the diameter is less than 100 Å, and then in pores from 100 to 50 Å diameter the reactive fraction increases from around 0.05 to 0.8. Since the silicon atoms on the surface, at a concentration of 4.6 OH nm⁻¹, must be separated by an average distance of about 4.7 Å, it can be visualized that the OH groups would not be brought appreciably closer to each other until the pore diameter becomes less than 100 Å (Figure 6.6). In a 50 Å diameter pore the radius is only about five times that of the Si–Si distance and the OH groups must be much closer together than on a flat surface.

After dehydration at high temperature there are, therefore, more hydrogen-bonded pairs of OH groups within such small pores than in larger ones.

Snyder and Ward propose that such a pair of OH groups is much more reactive than a single OH with a reactant such as $(CH_3)_3SiCl$. In effect, the one oxygen can begin to coordinate with the incoming silicon atom while the Cl is interacting with the hydrogen of the second OH:

$$
\begin{array}{c}
CH_3 \quad CH_3 \\
CH_3-Si-Cl \\
O\ H\cdot O\ H \\
Si\ \ Si
\end{array}
$$
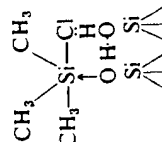
Table 6.2. Hydroxyl Group Retention in Gels

Temperature of Dehydration (°C)	Average Pore Diameter								
	10 Å			20 Å			27 Å		
	Area (m² g⁻¹)	Bound H₂O (%)	OH nm⁻²	Area (m² g⁻¹)	Bound H₂O (%)	OH nm⁻²	Area (m² g⁻¹)	Bound H₂O (%)	OH nm⁻²
115	400	6.5	10.8	540	6.1	7.5	450	3.8	5.6
300	480	4.4	6.1	500	4.3	5.7	500	4.0	5.3
600	375	3.4	6.0	400	2.9	4.8	420	2.3	3.6
700	280	1.5	3.6	340	1.7	3.3	210	1.1	3.5

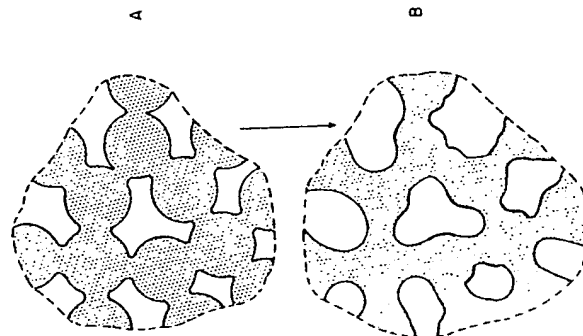Source. Dzis'ko, Vishnevskaya, and Chesalova (105).

This concerted effect is not possible with an isolated SiOH group and reaction requires a higher temperature.

In contrast with the above, the influence of surface curvature on hydroxyl groups has been calculated by Bakyrdzhiev (107) and data were obtained on four silica gels dehydrated at 300–600°C. He reported that *dehydration occurs at lower temperature in narrower pores*. This seems opposite to the above observations by Dzis'ko, Vishnevskaya, and Chesalova.

However, there is room for ambiguity here. The silica gel with narrower pores may have been formed from smaller silica particles. As shown in Figure 6.7, if the gel was not aged, the surface within the pores would consist mostly of small spherical particles with a *positive* radius of curvature. In this case the hydroxyl groups would be *less* strongly hydrogen bonded and therefore easier to remove as water. It is thus possible that on the same starting gel, an aging treatment can convert most of the inner silica surface from a positive to negative curvature, as in B. In such an aged gel the smaller the pores, the more stable the OH groups.

Rehydration

Studies by Young and Bursh (92, 102a) have clearly shown that water molecules are adsorbed only on the hydroxylated silica surface and not on the siloxane surface which is essentially hydrophobic. However, rehydration must involve adsorption of water as the first step, so that hydration probably occurs on siloxane oxygen sites

next to a silanol site. It was found that surfaces dehydrated up to 400–425°C were readily rehydrated, whereas above this temperature rehydration became progressively slower. At 425°C the surface retains about 2 OH nm⁻² or 40–45% of the original 4.6 OH nm⁻². The dehydrated siloxane sites are probably isolated. At this point the heat of adsorption of water per unit area of silica is at a maximum.

Rehydration of the partly dehydroxylated surface is catalyzed by alkali (108). However, high pH also promotes loss of surface area during prolonged contact with water. Addition of a little NH₄OH provides a safe pH range; certainly rehydration is slow below pH 5.

Snyder (10, 109) reports that rehydration of the partly dehydrated siloxane surface *even in liquid water* is exceedingly slow at 25°C. The silica must be heated in water at 95°C for several hours. However, this can be done only with heat-stabilized silicas of low surface area; high surface area powders would undergo drastic changes in structure and reduction in surface area under these conditions.

Rehydration of a highly dehydrated surface probably begins next to a free hydroxyl group since its characteristic infrared band becomes weaker (91). The idea, often stated, that the silica surface dehydrated at 1000°C cannot again be fully hydrated is not true, as shown by Agzamkhodzhaev et al. (110). They found that the more completely the surface was dehydrated, the longer the time required for rehydration. A silica aerogel that was heated at 1100°C for 10 hr, having a surface of 144 m² g⁻¹, retained only 0.06 OH nm⁻². After being boiled in water for 60 hr the surface area was still 108 m² g⁻¹ and rehydration of the surface was complete with 4.5 OH nm⁻². A surface dehydrated to 0.66 OH nm⁻² at 900°C for 10 hr required several years in water at ordinary temperature to become rehydrated.

It is likely that rehydration occurs only next to a hydroxyl group and that the hydroxylated area grows in patches as hydration proceeds along the boundary between hydroxylated and siloxane areas. It will therefore initially appear to be autocatalytic. Data by Volkov, Kiselev, and Lygin (111) seem to support this idea since on a highly dehydrated surface prepared at 900–1100°C, water was first chemisorbed by opening up strained siloxane bonds, forming silanol groups and water, then was adsorbed on these rather than on the siloxane surface. Further opening of siloxane bonds could occur only adjacent to these spots.

Surface Energies

Brunauer, Kantro, and Weise (103) reported the following values for the total surface energy (enthalpies) determined from the heat of dissolution in HNO₃–HF mixtures, of silica samples of different known surface areas with different states of dehydroxylation, all at 23°C:

	Energy (ergs cm⁻²)
Pure siloxane surface	259 ± 3
Pure silanol surface	129 ± 8
Heat of hydration	130 ± 7

Figure 6.7. Change from positive to negative curvature of the surface as silica gel is aged. A, unaged gel. Most of area in pores has a positive radius of curvature; B, aged gel. Most of the silica surface in pores has a negative radius of curvature. Slightly heavier lines show the areas with positive radius.

The Surface Chemistry of Silica

The heat of hydroxylation of siloxane surface to silanol at 23°C is 259 ± 13 cal g⁻¹ of water, or 4660 ± 230 cal mole⁻¹.

Kiselev (112) reported that when silica gels of different surface areas were heated at 300°C the hydroxylation of the surface decreased with increasing surface area. At the same time the surface energy of the silica increased. The effects were linear between the following approximate values:

Specific Surface Area $(m^2 g^{-1})$	SiOH (micromoles m^{-2})	Surface Energy $(ergs\ cm^{-2})$
100	5.0	170
700	3.3	200

As pointed out by Brunauer, Kantro, and Weise (103) and predicted by Iler (3), the total energy of the silanol surface is only slightly higher than the total surface energy of liquid water, 118.5 ergs cm⁻² at 25°C.

The development and status of the theory of surface free energy of solids and interfaces have been reviewed by Good (113). The theories relate to physical adsorption, wetting, and phase separations, but not to irreversible processes such as chemisorption.

Heat of Wetting of Silica Surface

It is obvious that if studies are made with microporous silicas with pores of different sizes, very little can be concluded about the nature of the surfaces by measuring the heat of wetting. Only nonmicroporous silicas can be considered.

Based on early data on the heat of wetting of various silica powders with different degrees of surface hydration, as measured by Patrick (114), Iler (3) extrapolated the following values.

	Heat of Wetting $(ergs\ cm^{-2})$
Silanol surface	190
Siloxane surface	130
Difference	60

However, there was no assurance that some micropores were not present.

Taylor, Hockey, and Pethica (84) have obtained data on the heat of immersion in water of an annealed, rehydrated silica surface at various stages of dehydroxylation at temperatures where no sintering or change in surface area occurs. For the fully hydroxylated material it was 160 ± 3 ergs cm⁻², and this was independent of the area of the silica from 8 to 150 m² g⁻¹.

Nature of the Silica Surface

The heat of immersion of silicas dehydrated at various temperatures is very confusing unless the silica is first annealed at 700°C to eliminate micropores or surface Si_2OH groups, and then rehydrated. Otherwise the heat of immersion differs at different temperatures (27 vs. 45°C) as shown by Taylor, Hockey, and Pethica (84). This is at least partly due to the different arrangements of SiOH groups on the surface which can undergo change upon being wetted. On the other hand, the annealed silica, rehydrated, has a stable surface that has the same heat of wetting at 27 and 45°C, and this increases with the number of hydroxyl groups on the surface:

OH nm^{-2}	Heat of Immersion (Approximate) $(ergs\ cm^{-2})$
0	117 (extrapolated)
2	122
3	130
4.7	160

This value of 117 ergs cm⁻² for the heat of wetting of the siloxane surface is more dependable and somewhat lower than the value of 130 ergs cm⁻² calculated by Iler. Other higher values obtained by other workers can probably be explained by the fact that there were micropores present or the silica surface had not been stabilized by annealing. Taylor, Hockey, and Pethica show that the heat of wetting of the surface of unannealed silica at maximum hydroxylation of 4.7 OH nm⁻² may approach 200 ergs cm⁻².

There are many factors affecting the heat of immersion of nonannealed hydroxylated silicas that remain to be investigated. For example, Taylor, Hockey, and Pethica found that dehydration in vacuo resulted in a higher heat of wetting than heating in air—probably because in the latter case the steam, which was not immediately drawn off, promoted rearrangements of surface SiOH groups.

A differential wetting calorimeter was developed for measuring heats of immersion of solids by Tyler et al., (115). Well characterized pyrogenic silicas (Aerosil) were used for heat of wetting experiments in water and benzene.

The nonwetting or hydrophobic character shown by the siloxane surface when contacted with liquid water led Laskowski and Kitchener (116) to the conclusion that the work of adhesion of water to a solid surface consists of three terms:

1. Dispersion forces (van der Waals).
2. Hydrations of nonionic polar sites, that is, bonding with SiOH groups.
3. Ionization.

On silica, the second factor controls wettability. The contact angle and zeta potential between water and vitreous silica was measured on the surface, which had been made hydrophobic with $(CH_3)_3SiCl$. After a time the original hydrophobic sur-
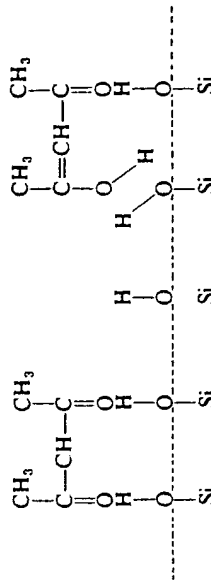
practical merits of gel adsorbents. The extensive review of the physical adsorption of gases and vapors in the first part of Chapter 5 should be referred to at this point. Only a few aspects of the subject are included here and these are restricted generally to silica surfaces free from micropores.

Numerous investigations make it clear that adsorption of polar molecules or aromatic compounds through pi bonds occurs most strongly on silanol groups that are not already hydrogen-bonded with neighbors. Thus on silica dehydrated at 500°C on which there remain about 2.7 OH nm^{-2}, one $C_2H_5NH_2$ is adsorbed per OH group at room temperature (121). Ammonia is similarly adsorbed stoichiometrically on SiOH groups according to Bastik (122).

For a brief summary of the phenomenon of adsorption on various surfaces, especially silica, reference should be made to the short monograph by Kiselev (123). The role of hydrogen bonding in adsorption of different classes of compounds was revealed by infrared absorption studies, for example, diethyl ether (124), pyrrole (125), and t-BuOH (126).

The strength of the hydrogen bond is indicated by the shift in the infrared adsorption band of the OH due to stretching. Sempels and Rouxhet (127) compared the electron donor characteristics of a series of weak hydrogen bonding agents in this way. They showed that the hydrogen bonds are the same in solution as on the solid surface.

The effect of adsorption of a molecule with different configurations such as ClC_2H_4Cl was to increase the cis-trans ratio from 1.0 in $CHCl_3$ solution to 1.9 or the silica surface (128). With acetylacetone it was the enol form that was involved in the hydrogen bond. This observation suggests that the molecular form favored at the surface is the one that provides the greatest number of hydrogen bridges:

$$
\begin{array}{llll}
CH_3 & CH_3 & CH_3 & CH_3 \\
C-CH-C=O & & C-CH-C=O & \\
\quad H-O & & \quad O\;H & H\;O \\
\quad O & & \quad O & \quad O \\
\quad Si & Si & Si & Si
\end{array}
$$

Steric hindrance can prevent hydrogen bonding and adsorption on the surface a in the case of 2-chloropyridine, where the large chlorine atom apparently prevent close approach (129).

Activated Al_2O_3–SiO_2 gel does not adsorb pyridine vapor as strongly as silic does. The nature of adsorption on silica–alumina has been well reviewed by Hair (9) who points out that on an activated silica–alumina gel the only hydroxyl groups ar SiOH. These must therefore be fewer per unit area than on hydroxylated silica an thus adsorb less pyridine.

The adsorption of ammonia on the silica surface is not a simple process accordin to Biznakov and Polikarova (130). An increasing amount of irreversibly boun ammonia remains below 70°C. According to Boyle and Gaw (131) the adsorption i

face became wetted (contact angle zero) even though methyl groups were still on the surface. After removing physically adsorbed water the surface was again hydrophobic. (It is likely the surface was not fully covered with methyl groups.) When covered with close-packed hydrocarbon groups, the surface shows no such reversible phenomenon; this has been proved in the case of estersils, where a surface covered with closely packed butyl groups remains hydrophobic for months in water.

The heat of wetting by polar liquids (117, 118) decreases as the silica surface is dehydroxylated. With a nonpolar liquid like heptane the heat of wetting increases. Even in the case of methanol the heat of wetting on the completely dehydroxylated surface is 75 ergs cm^{-2} as compared to 50 for water. It appears that the heat of wetting depends on the association of the polar groups in the organic molecule with the polar silanol surface and the association of the hydrocarbon portions of the molecule with the hydrophobic siloxane surface. A fully hydroxylated silica surface immersed in water shows no hydrophobic characteristics.

PHYSICAL ADSORPTION OF NONIONIC LOW MOLECULAR WEIGHT COMPOUNDS

Physical adsorption studies on silica during the past half-century must number 1000 or more. In this section only typical examples of nonionic physical adsorption are discussed. Ionic adsorption is dealt with later.

The methods and techniques for studying adsorption such as infrared absorption, nuclear magnetic resonance, and dielectric measurements are not described here but may be learned through references.

Hydrogen bond formation between electronegative atoms or pi electrons of adsorbate molecules and the hydrogen atoms of the silanol groups on the silica surface plays a major role in adsorption of molecules from the vapor state and from nonaqueous solution. It also is a major factor in adsorption from aqueous solution of nonionizing types of molecules. This role of the hydrogen bond has been reviewed by Hair (9), Little (119), and Kiselev and Lygin (120).

Adsorption of Vapors

Reversible adsorption implies that only intermolecular physical forces are involved and that desorption has a very low activation energy. This includes molecules which are hydrogen bonded to the surface. However, there may be cases where there are several points of hydrogen-bonded attachment to the surface, such as with $C_2H_5OC_2H_4OC_2H_4OC_2H_5$, where desorption may appear essentially irreversible, or at least the adsorption follows a Langmuir-type isotherm. Some multiply-bonded surface complexes may be so stable that they might be considered as essentially chemisorbed.

Adsorption of gases and vapors on gels and powders has been studied mainly as a method of characterizing the solids. Also, such data are essential to evaluating the